

ANODIZATION-ADAPTED ALUMINUM ALLOY AND
PLASMA-TREATING APPARATUS MADE THEREOF

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to an anodization-adapted aluminum alloy and a plasma-treating apparatus made of the anodization-adapted aluminum alloy. More
10 particularly, it relates to such an aluminum alloy and plasma-treating apparatus for service in both corrosion and plasma treatment environments.

2. Description of the Related Art

In a prior art plasma-treating apparatus for
15 use in producing semiconductors and liquid crystal, corrosive gases and irradiating plasma heavily damage non-processed aluminum. In addition, metallic elements scattered from the material adversely affect an article to be processed such
20 as a silicon wafer. In order to overcome such inconveniences, materials as defined by the JIS Standard, such as a 5000-series aluminum alloy (hereinafter called a "5000-series alloy") and a 6000-series aluminum alloy (hereinafter called a
25 "6000-series alloy"), are in common uses, in which

instance, the 5000- and 6000-series alloys are subjected to hard anodized aluminum treatment (hereinafter referred to as "anodization").

In recent years, causes such as micro-wiring patterns in a semi-conductor device, high-density plasma to be used, and high-corrosive gases to be used have rendered it conspicuous as an important issue to avoid deterioration and contamination of members used under plasma environments.

Fig. 5 illustrates amounts of impure elements contained in aluminum alloys, in comparison with aluminum having a high purity of 99.9 wt% (3N) or greater.

As illustrated in Fig. 5, commercially available 5052- and 6061-alloys contain considerable amounts of impure elements, when compared with the high-purity aluminum alloy. In the 5000- and 6000-series alloys, the 5052- and 6061-alloys are most widely used as materials of a plasma electrode plate and a plasma chamber. These impure elements are likely to cause defects in an anodized film. In addition, the impure elements may reside in the anodized film. This causes contamination because the impure elements residing in the anodized film are likely to fall onto an

article to be processed such as a silicon wafer during plasma treatment.

In order to avoid lodging the impure elements in the anodized film, it is believed that aluminum having a high purity of 3N or greater is preferably used as a material. However, the plasma electrode plate and the plasma chamber need the strength of some 200 to 300 N/mm², which is similar to the strength of the 5000- or 6000-series alloy. Accordingly, the high-purity aluminum smaller in strength than the 5000- and 6000-series alloys is difficult to solely employ.

In order to meet such requirements under the plasma circumstance, it has been proposed to use an aluminum alloy having Mg and Si added to high-purity aluminum (refer to published Japanese Patent Application Laid-Open No. 10-88271) and an aluminum alloy having Mg, Si, and Cu added to the high-purity aluminum (refer to published Japanese Patent Application Laid-Open No. 2001-220637).

The hitherto proposed aluminum alloys satisfy, to a certain degree, the above requirements under the plasma environment. In such aluminum alloys, the added Mg and Si precipitate Mg₂Si to increase the strength of the high-purity aluminum.

In this instance, minute Mg_2Si is precipitated in the anodized film.

However, the minute Mg_2Si precipitated in the film forms air gaps in the film. The formed air gaps
5 inconveniently render the film susceptible to spallation during plasma irradiation, and thus inconveniently reduce the corrosion resistance of the aluminum alloy.

In the aluminum alloy taught in the published
10 Japanese Patent Application Laid-Open No. 2001-220637 as previously discussed, the added Cu results in high-density Cu around the precipitated Mg_2Si to form air gaps during anodization. The formed air gaps alleviate the occurrence of cracks in the
15 film. However, as previously discussed, the film is preferably devoid of such void spaces.

In general, members used under the plasma circumstance are costly. Accordingly, each of the costly members is removed when being worn to some
20 degree. The film is stripped from the worn member. The worn member free of the film is again anodized, thereby forming a new film on the re-anodized member. In this way, the members are often reused. In the aluminum having Mg_2Si precipitated, however,
25 components under the plasma circumstance are heated

to coarsen Mg_2Si in the material. The coarsened Mg_2Si inconveniently results in defects in the film and reduced corrosion resistance of the aluminum during anodization-caused film formation.

5 SUMMARY OF THE INVENTION

In view of the above, an object of the present invention is to provide an anodization-adapted aluminum alloy having good corrosion resistance and operable to suppress the occurrence of cracks in
10 a film on the anodization-adapted aluminum alloy during plasma irradiation thereon under a plasma-processing environment, and to provide a plasma-treating apparatus made of the anodization-adapted aluminum alloy as discussed
15 above.

In order to achieve the object, a first aspect of the present invention provides an anodization-adapted aluminum alloy containing 2.0 to 3.5 wt% Mg and the remainder of 99.9 wt% or greater
20 high-purity aluminum.

A second aspect of the present invention provides an anodization-adapted aluminum alloy containing 2.0 to 3.5 wt% Mg, 0.004 to 0.01 wt% Ti, and the remainder of 99.9 wt% or greater high-purity
25 aluminum.

In order to achieve the above object, a third aspect of the present invention provides a plasma-treating apparatus made of an anodization-adapted plasma alloy, designed to allow an article to be processed to experience predetermined treatment in a vacuum chamber, using either plasma or active species that are occurred by the plasma, the plasma-treating apparatus characterized in that one or more kinds of components selected from among the vacuum chamber and components provided in the vacuum chamber comprise an aluminum alloy member formed by an anodized aluminum alloy that contains 2.0 to 3.5 wt% Mg and the remainder of 99.9 wt% or greater high-purity aluminum.

A fourth aspect of the present invention provides a plasma-treating apparatus made of an anodization-adapted plasma alloy, designed to allow an article to be processed to experience predetermined treatment in a vacuum chamber, using either plasma or active species that are occurred by the plasma, the plasma-treating apparatus characterized in that one or more kinds of components selected from among the vacuum chamber and components provided in the vacuum chamber

comprise an aluminum alloy member formed by an anodized aluminum alloy that contains 2.0 to 3.5 wt% Mg, 0.004 to 0.01 wt% Ti, and the remainder of 99.9 wt% or greater high-purity aluminum.

5 Mg is added to the high-purity aluminum alloy in order to provide a solid solution-hardened and improved corrosion-proof material.

More specifically, a difference in atomic radius between Mg and Al provides solution treatment
10 of Mg, thereby providing improved material strength. In addition, the improved material strength caused by the solution-treated Mg makes it feasible to form a film free of void spaces, not encouraging Mg_2Si precipitation. This feature provides an improved
15 corrosion-proof material.

Moreover, the alloy having Mg added thereto forms MgF_2 in a CVD (chemical vapor deposition) apparatus that uses CF-series plasma gases. As a result, film destruction can be suppressed.

20 As discussed above, in order to afford improved material strength, Mg is added to aluminum to practice the solution treatment of Mg in the aluminum. The Mg content is limited to be 2.0 to 3.5 wt%. Mg in an amount of 2.0 wt% or smaller is
25 insufficient for the improved material strength,

and therefore 2.0 wt% or greater Mg must be added.
3.5 wt% or greater Mg results in a poor
corrosion-proof material as well as a poor
corrosion-proof film, and therefore 3.5 wt% or
5 smaller Mg must be added.

Ti as well as Mg is added to the high-purity
aluminum alloy in order to provide a material having
minute crystal grains.

Adding Mg to the material coarsens the
10 crystal grains of the material. The coarsened
crystal grains differ in crystal directionality
therebetween. This phenomenon grows an anodized
film at different speeds, and consequently permits
plasma to non-uniformly damage such formed film.
15 In order to suppress such objectionable results,
the crystal grains must be micro-structured. To
achieve this purpose, Ti is added to the aluminum
alloy.

As described above, Ti is added to provide
20 minute material grains. The Ti content is limited
to be 0.004 to 0.01 wt%. Ti in an amount of 0.004
wt% or smaller is insufficient for the minute
crystal grains, and therefore 0.004 wt% or greater
Ti must be added. Ti is an alloy to be anodized.
25 0.01 wt% or greater Ti in excess of a solution

treatment limit in the aluminum alloy forms an anodized film in a manner similar to what aluminum does. As a result, an anodized non-uniform film having varying thickness is produced. Therefore,
5 0.01 wt% or smaller Ti must be added.

An anodization-adapted aluminum alloy according to the present invention and a plasma-treating apparatus fabricated of the anodization-adapted aluminum alloy according to
10 the present invention exhibits good corrosion resistance, and operatively inhibits the occurrence of cracks in the anodized film on the anodization-adapted aluminum alloy during plasma irradiation thereon.

15 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a composition of an aluminum alloy as an example of an anodization-adapted aluminum alloy according to the present invention;

20 Fig. 2 illustrates corrosion area ratios of respective anodized films of the anodization-adapted aluminum alloy according to the present invention, a 5052-alloy, and a 6061-alloy after each of the anodized films is
25 subjected, for 96-hours, to both salt-water spray

and a CASS test;

Fig. 3 illustrates photographs of the respective anodized films of the anodization-adapted aluminum alloy according to the present invention, the 5052-alloy, and the 6061-alloy, in which the photographs show the anodized films before plasma irradiation thereon, and after the plasma irradiation thereon using a CF_4 -gas for six hours in a plasma-treating apparatus;

Fig. 4 illustrates the thickness of each of the anodized films of the aluminum alloy according to the present invention, the 5052- and 6061-alloys before the plasma irradiation thereon, and after the plasma irradiation thereon using the CF_4 -gas for six hours in the plasma-treating apparatus; and

Fig. 5 illustrates amounts of impure elements contained in aluminum alloys, in comparison with aluminum having a high purity of 99.9 wt% (3N) or greater.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The best mode of the present invention is now described with reference to the accompanying drawings.

Fig. 1 illustrates a composition of an

aluminum alloy as an example of an anodization-adapted aluminum alloy according to the present invention.

The aluminum alloy having a composition as
5 illustrated in Fig. 1 is obtained by casting molten aluminum into a billet or slab according to a semi-continuous casting process. The molten aluminum has a composition adjusted by: adding Mg having a purity of 99.95 wt% or greater to Al having
10 a purity of 99.9 wt% or greater; and subsequently adding Ti thereto in the form of mother alloys such as Al-Ti and Al-Ti-B.

The following discusses corrosion resistance of the anodization-adapted aluminum
15 alloy according to the present invention as provided above, and further discusses the occurrence of cracks in a film on the same aluminum alloy.

Fig. 2 illustrates corrosion area ratios of respective anodized films of the
20 anodization-adapted aluminum alloy according to the present invention, a 5052-alloy, and a 6061-alloy after each of the anodized films is subjected, for 96-hours, to both salt-water spray and a CASS test.

25 In Fig. 2, signs "A", "B", and "C" denote

the anodization-adapted aluminum alloy according to the present invention, the 5025-alloy, and the 6061-alloy, respectively. In addition, signs "(a)" and "(b)" denote the salt-water spray and the CASS test, respectively. A plasma-treating apparatus has an issue of corrosion resistance against corrosive gases. In general, it is very difficult to examine toxic properties of the corrosive gases used in the plasma-treating apparatus. It is also very difficult to examine actually used gases. Accordingly, both of the salt-water spray and the CASS test evaluate the corrosion resistance of each of the anodized films of the anodization-adapted aluminum alloy according to the present invention and the 5052-and 6061-alloys.

As evidenced by Fig. 2, results from the salt-water spray show that the anodized film of the aluminum alloy according to the present invention has a corrosion area ratio of only 1.11%, while the anodized films of the 5052- and 6061-alloys have corrosion area ratios of 13.89% and 8.16%, respectively. Consequently, the anodization-adapted aluminum alloy according to the present invention is superior in corrosion resistance to the other alloys. Results from the

CASS test show that the anodized film of the aluminum alloy according to the present invention has a corrosion area ratio of only 3.26%, while the anodized films of the 5052- and 6061-alloys have
5 corrosion area ratios of 14.26% and 11.29%, respectively. Consequently, the anodization-adapted aluminum alloy according to the present invention surpasses the other alloys in corrosion resistance.

10 Fig. 3 illustrates photographs of the respective anodized films of the anodization-adapted aluminum alloy according to the present invention, the 5052-alloy, and the 6061-alloy. The photographs show the anodized films
15 before plasma irradiation thereon, and after the plasma irradiation thereon using a CF_4 -gas for six hours in the plasma-treating apparatus. In Fig. 3, signs "A", "B", and "C" denote the anodization-adapted aluminum alloy according to
20 the present invention, the 5052-alloy, and the 6061-alloy, respectively. In addition, signs "(c)" and "(d)" show post-plasma irradiation and pre-plasma irradiation, respectively.

As evidenced by Fig. 3, the anodized film
25 of the anodization-adapted aluminum alloy

according to the present invention is found to be more resistant to crack than the anodized films of the 5052- and 6061-alloys when the plasma is irradiated onto these three different alloys.

5 Fig. 4 illustrates the thickness of each of the anodized films of the aluminum alloy according to the present invention, the 5052- and 6061-alloys before the plasma irradiation thereon, and after the plasma irradiation thereon using the CF_4 -gas
10 for six hours in the plasma-treating apparatus. In Fig. 4, signs "A", "B", and "C" denote the anodization-adapted aluminum alloy according to the present invention, the 5052- and 6061-alloys, respectively. In addition, signs "(e)", "(f)", and
15 "(g)" denote film thickness before the plasma irradiation, film thickness after the plasma irradiation, and a reduction in film thickness during the plasma irradiation.

As evidenced by Fig. 4, the plasma
20 irradiation reduces the thickness of the anodized film of the 5052-alloy from $56.7 \mu\text{m}$ to $43.3 \mu\text{m}$. This means that the anodized film is reduced in thickness by an amount of $13.4 \mu\text{m}$. Similarly, the plasma irradiation reduces the thickness of the anodized
25 film of the 6061-alloy from $54 \mu\text{m}$ to $37.8 \mu\text{m}$. That

is, the anodized film is reduced in thickness by an amount of $16.2 \mu\text{m}$. Meanwhile, the plasma irradiation reduces the thickness of the anodized film of the anodization-adapted aluminum alloy according to the present invention from $52.7 \mu\text{m}$ to $44 \mu\text{m}$. That is, the anodized film is reduced in thickness by an amount of only $8.7 \mu\text{m}$. Consequently, the anodization-adapted aluminum alloy according to the present invention provides an anodized film immune to the plasma irradiation to a certain degree.

An Mg_2Si -precipitating alloy material worked by forging and rolling must be subjected to solution heat treatment and subsequently an aging process. In contrast, the anodization-adapted aluminum alloy according to the present invention does not need any heat treatment. Accordingly, the anodization-adapted aluminum alloy according to the present invention is superior in cost as well as quenching that is involved in heat-treated hard alloys such as the Mg_2Si -precipitating alloy material.

Elements such as Cr and Mn are often added to the 5052- and 6061-alloys in order to provide a material having minute crystal grains. In this

instance, significant amounts of such elements must be added to provide sufficiently minute grains. However, the presence of the elements such as Cr and Mn are objectionable in a semiconductor because
5 these are named as heavy metal contamination elements. In contrast, the anodization-adapted aluminum alloy according to the present invention has a very minute amount of Ti added thereto. In addition, Ti less involves heavy metal
10 contamination in the semi-conductor. This feature sufficiently limits the plasma-caused scattering of heavy metals from the anodized film.